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MEMORANDUM FOR PRS

FROM: PROI (TI) (STINFO)

28 May 1999

SUBJECT: Authorization for Release of Technical Information, Control Number: **AFRL-PR-ED-TP-FY99-0113**
C.W. Larson, "Kinetics of Boron Carbon HEDM"

Presentation **HEDM Conference** **(Statement A)**

formation/reaction

Kinetics of Boron Carbon HEDM

C. W. Larson,
Air Force Research Laboratory,
Edwards AFB, CA 93524-7680

HEDM Contractors' Conference
Cocoa Beach, FL
7 June - 11 June 1999

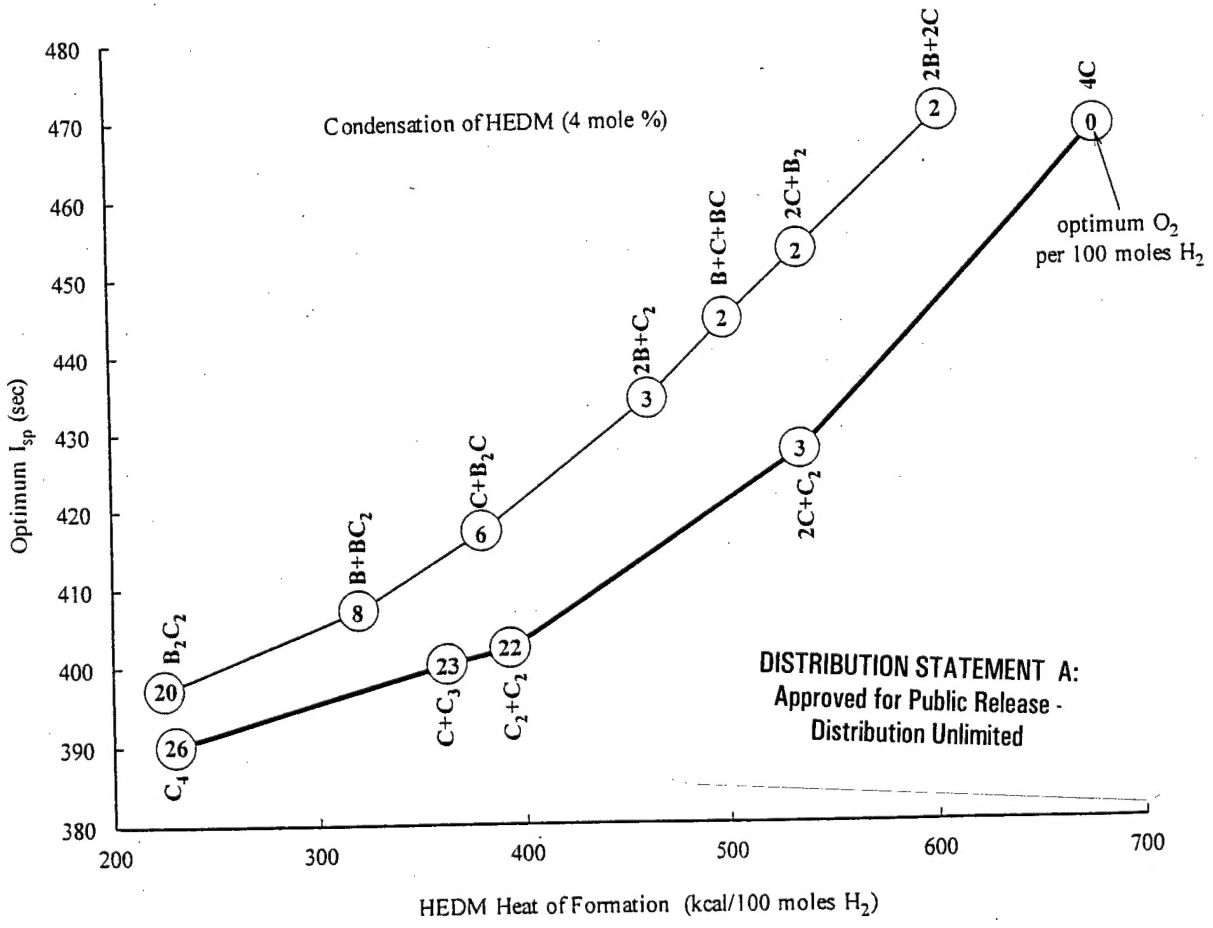


Figure 1. Specific impulse of HEDM containing 4 mole percent equivalent atom density in solid hydrogen with various stages of condensation. Numbers inside circles denote the optimum moles of O_2 per 100 moles of H_2 that produces the maximum Isp for the indicated compositions. The calculations are based on the standard rocket operating conditions, 1000 psi combustion pressure and 1 atm nozzle exit pressure, which produce 389 sec with liquid oxygen/liquid hydrogen propellant. The propellant composed of 4 mole percent C-atoms produces maximum Isp with no oxygen. If the atoms condense to 1 mole percent C4, the Isp drops to the baseline 389 sec value.

Objective - 5% atoms in cryogenic matrix

Approach

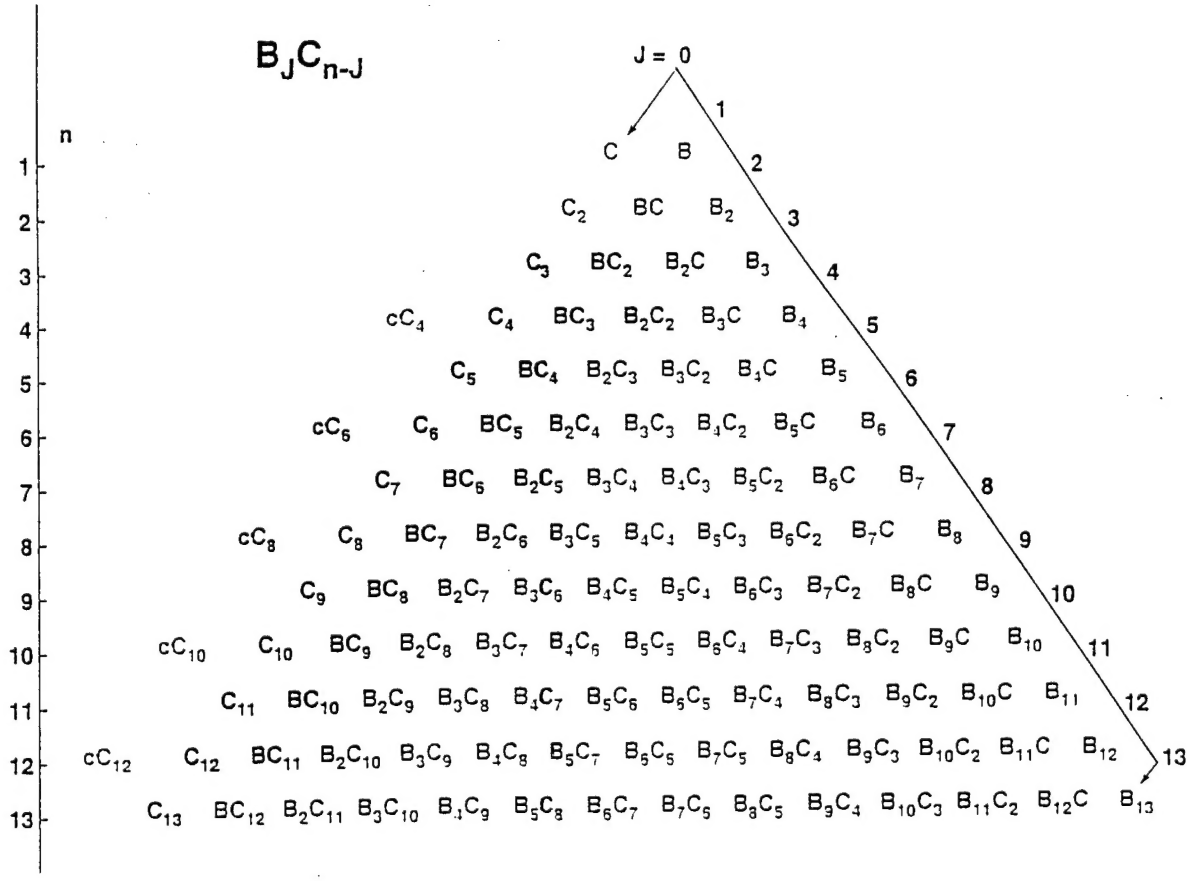
1. FTIR spectroscopy of B_JC_{n-J} clusters isolated in 10 K argon matrix

2. Ab-initio calculations of cluster
   (a) normal mode frequencies and frequency shifts of their isotopomers
   (b) infrared absorption intensities (km mol^{-1})

3. Measurement of cluster distributions produced upon deposition and after annealing . Absolute column densities (molecules cm^{-2}) from Beer's Law

$$<\rho_i l> = \frac{A_{exp}}{I_{theory}} N$$

$$A_{exp} = -\int_{\nu} \ln\left[\frac{E_t(\nu)}{E_0(\nu)}\right] d\nu$$



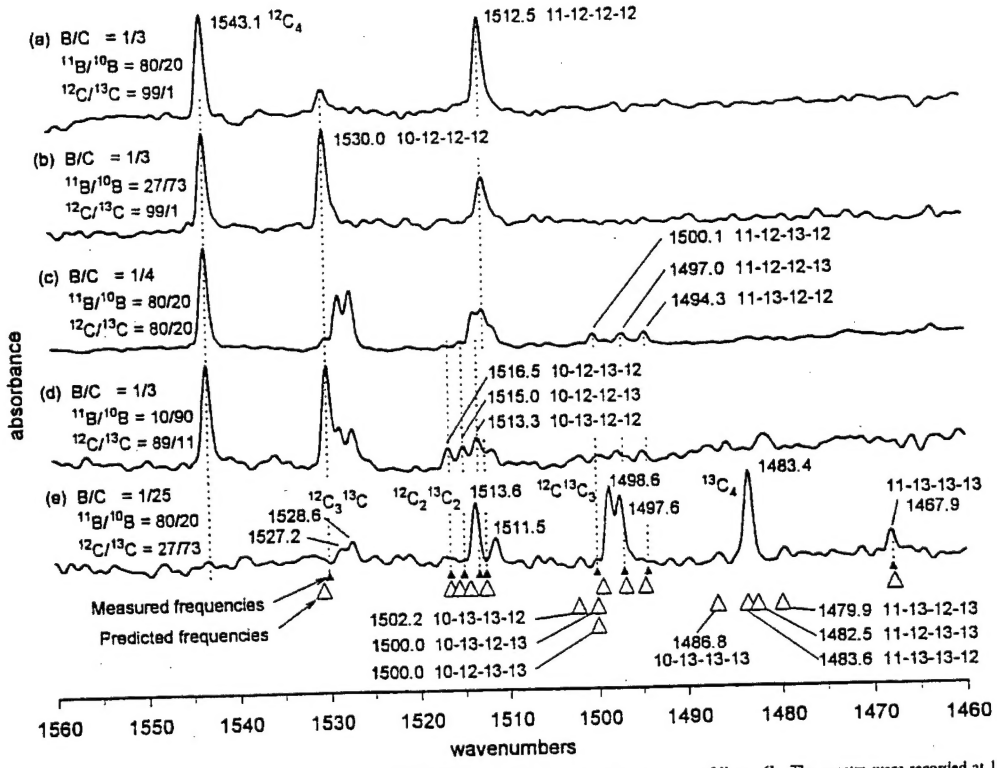


FIG. 1. FTIR spectra of the $\nu_2(\sigma)$ mode of isotopomers of linear BC_3 and the $\nu_3(\sigma_u)$ mode of isotopomers of linear C_4. The spectra were recorded at 10 K after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BC_3 isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

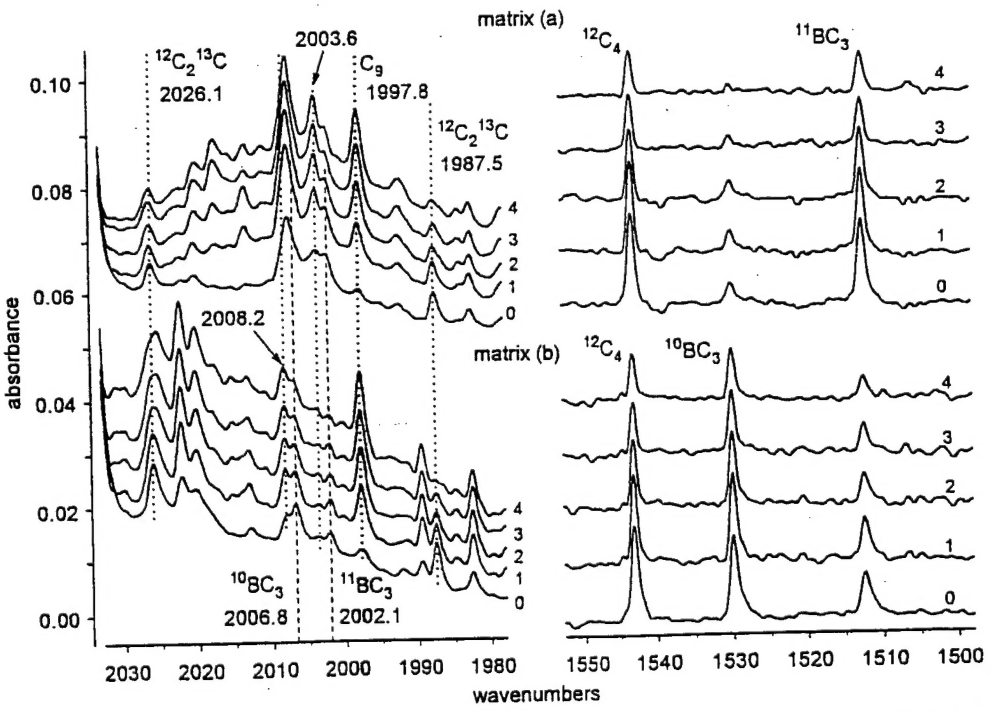


FIG. 2. Spectra obtained from matrix (a) [$^{11}B/^{10}B = 4/1$] and matrix (b) [$^{11}B/^{10}B = 1/2.7$] showing correlation upon annealing of the $\nu_1(\sigma)$ bands of $^{10}BC_3$ and $^{11}BC_3$ at 2006.8 and 2002.1 cm^{-1} with the $\nu_2(\sigma)$ bands at 1530.0 and 1512.5 cm^{-1}. The spectra labeled "0" are from the originally deposited matrix. Labels "1" to "4" indicate spectra recorded after the first through fourth annealing as follows: (1) 27.5 K for 150 s, (2) 30.0 K for 75 s, (3) 32.5 K for 45 s, (4) 35.0 K for 30 s. Frequency and absorbance scales are identical for all spectra. The plotted absorbance is $-\log_{10}$ of the transmittance. To facilitate comparisons between matrices, the absorbance of the matrix (b) spectra are multiplied by 1.4.

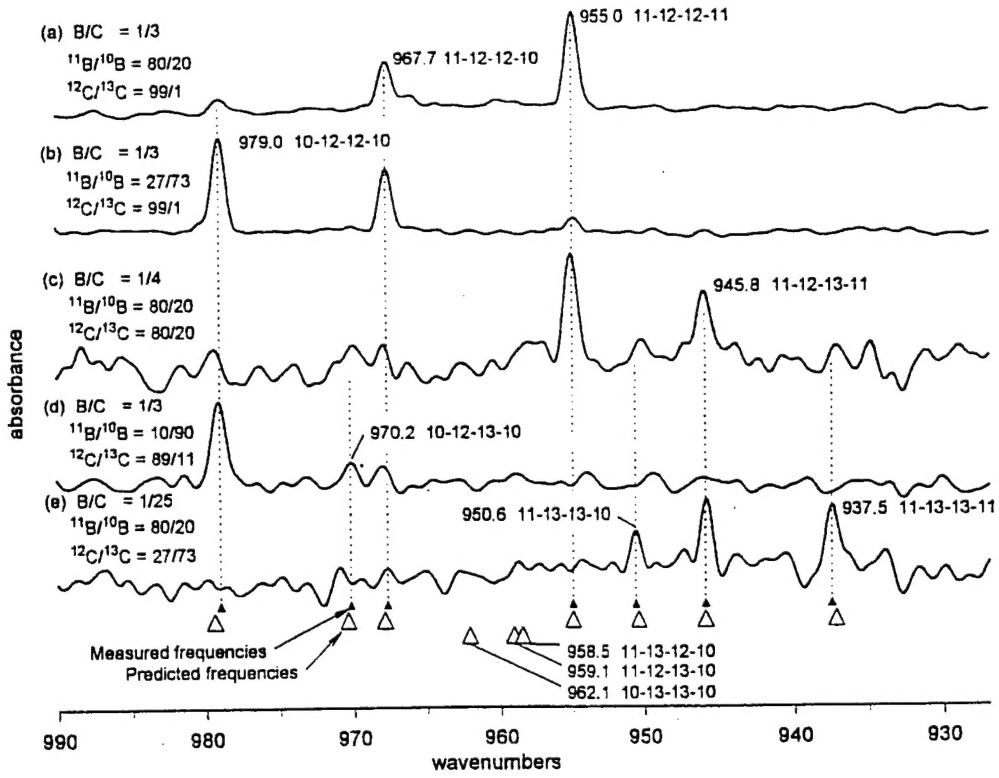
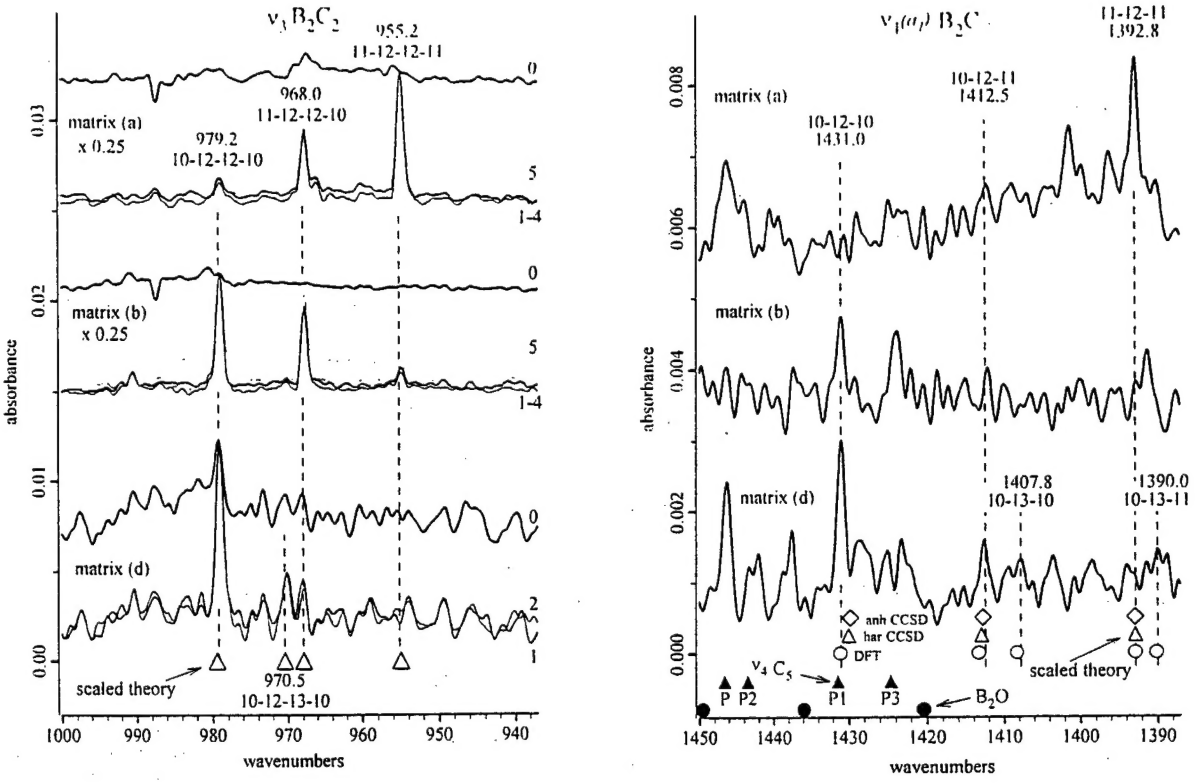


FIG. 3. FTIR spectra of the $\nu_3(\sigma_u)$ mode of isotopomers of linear BCCB. The spectra were recorded after annealing the matrices with the indicated compositions at 27.5 K for 150 s. The large open triangles at the bottom show the predicted frequencies of linear BCCB isotopomers (as explained in the text) and small filled triangles show measured isotopomer frequencies.

TABLE IV. Experimental B_2C_2 isotopomer frequency patterns. Frequencies and frequency intervals (cm^{-1}) in triplet bands of B_2C_2 isotopomers.

Boron isotope triplets				Carbon isotope triplets			
		Intervals				Intervals	
Isotopomer	Freq.	Short	Long	Isotopomer	Freq.	Short	Long
$^{10}B_2\,^{12}C_2$	979.0	11.3	24.0	$^{10}B_2\,^{12}C_2$	979.0	8.8	(16.7)[a]
$^{10,11}B_2\,^{12}C_2$	967.7	12.7		$^{10}B_2\,^{12,13}C_2$	970.2	(7.9)[a]	
$^{11}B_2\,^{12}C_2$	955.0			$^{10}B_2\,^{13}C_2$	(962.3)[a]		
$^{10}B_2\,^{12,13}C_2$	970.2	(11.5)[a]	24.4	$^{10,11}B_2\,^{12}C_2$	967.7	(9.0)[a]	17.1
$^{10,11}B_2\,^{12,13}C_2$	(958.7)[a]	(12.9)[a]		$^{10,11}B_2\,^{12,13}C_2$	(958.7)[a]	(8.1)[a]	
$^{11}B_2\,^{12,13}C_2$	945.8			$^{10,11}B_2\,^{13}C_2$	950.6		
$^{10}B_2\,^{13}C_2$	(962.3)[a]	(11.7)[a]	(24.8)[a]	$^{11}B_2\,^{12}C_2$	955.0	9.2	17.5
$^{10,11}B_2\,^{13}C_2$	950.6	13.1		$^{11}B_2\,^{12,13}C_2$	945.8	8.3	
$^{11}B_2\,^{13}C_2$	937.5			$^{11}B_2\,^{13}C_2$	937.5		

[a]Frequencies and intervals in parentheses were interpolated or extrapolated from measured quantities.



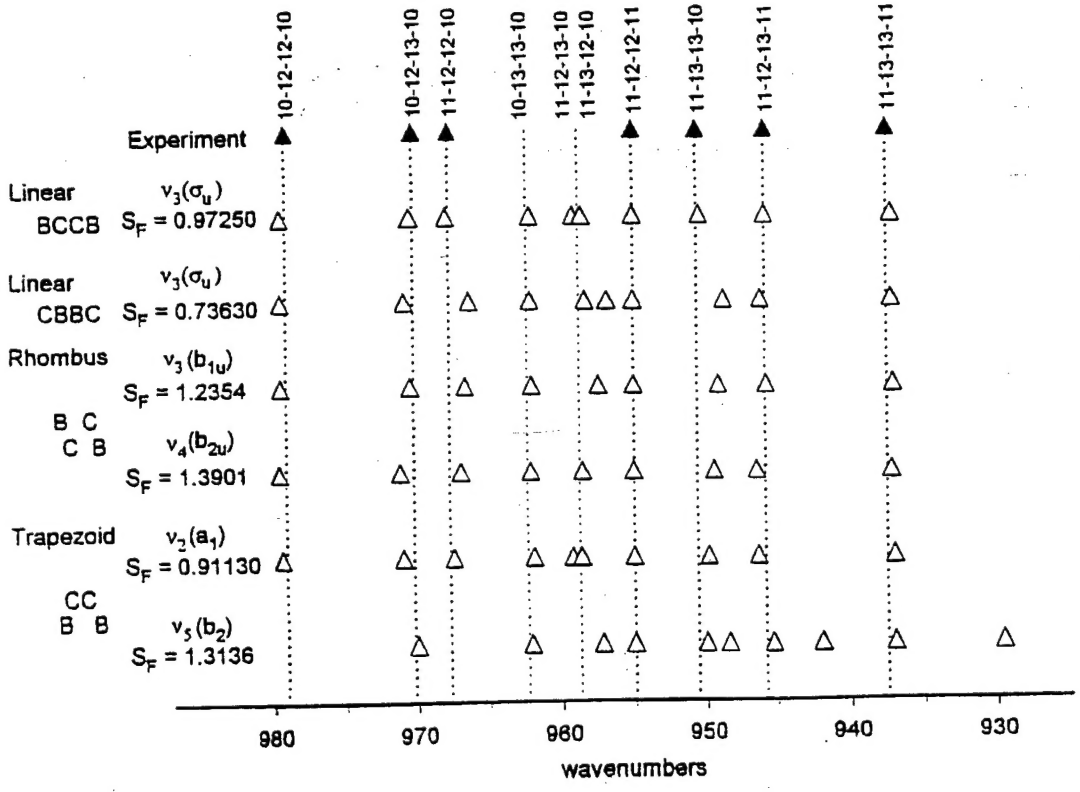
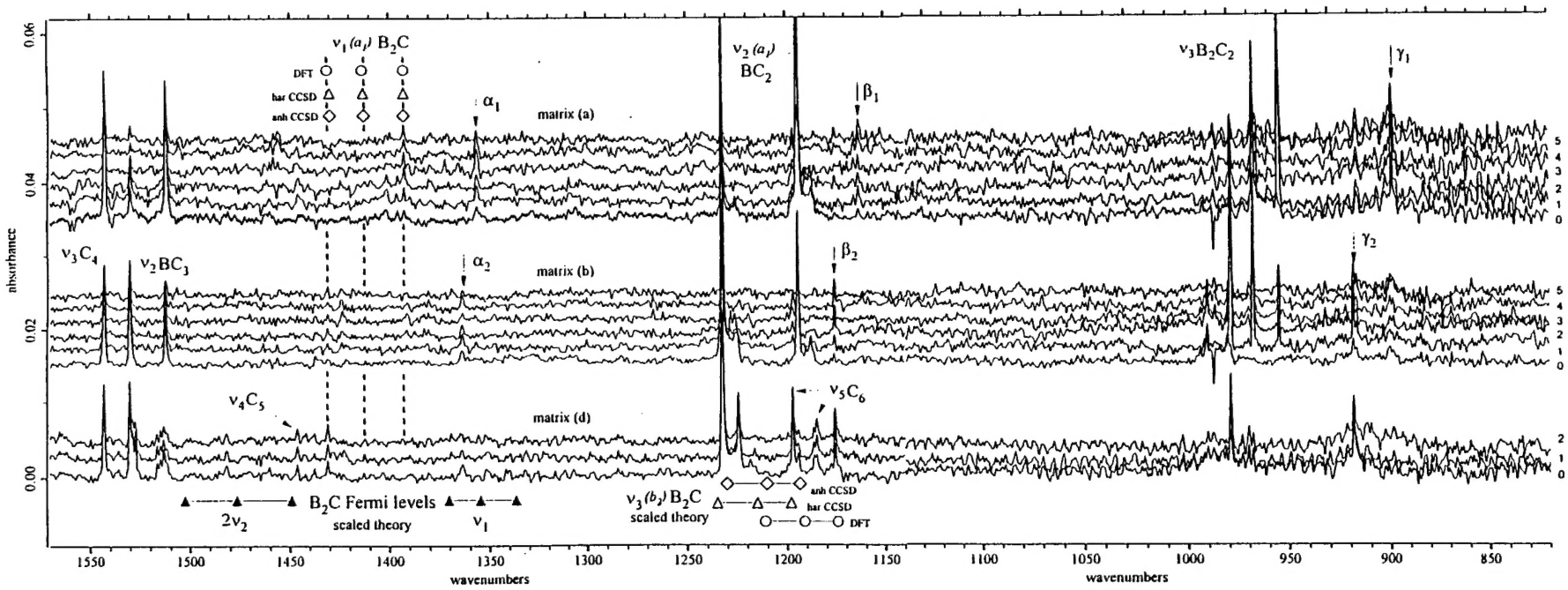


FIG. 4. Comparison of experimental isotopomer frequencies to scaled theoretical isotopomer frequencies for the most intense modes of four B_2C_2 geometries as calculated by Rittby. Ref. 5.


absorbance
0.06
0.04
0.02
0.00
$\nu_1 (a_1)$ B_2C
DFT
har CCSD
anh CCSD
α_1
matrix (a)
$\nu_2 (a_1)$
BC_2
β_1
$\nu_3B_2C_2$
γ_1
ν_3C_4
ν_2BC_3
α_2
matrix (b)
β_2
γ_2
ν_4C_5
matrix (d)
ν_5C_6
B_2C Fermi levels
$2\nu_2$
scaled theory
ν_1
$\nu_3 (b_2)$ B_2C
scaled theory
anh CCSD
har CCSD
DFT
1550
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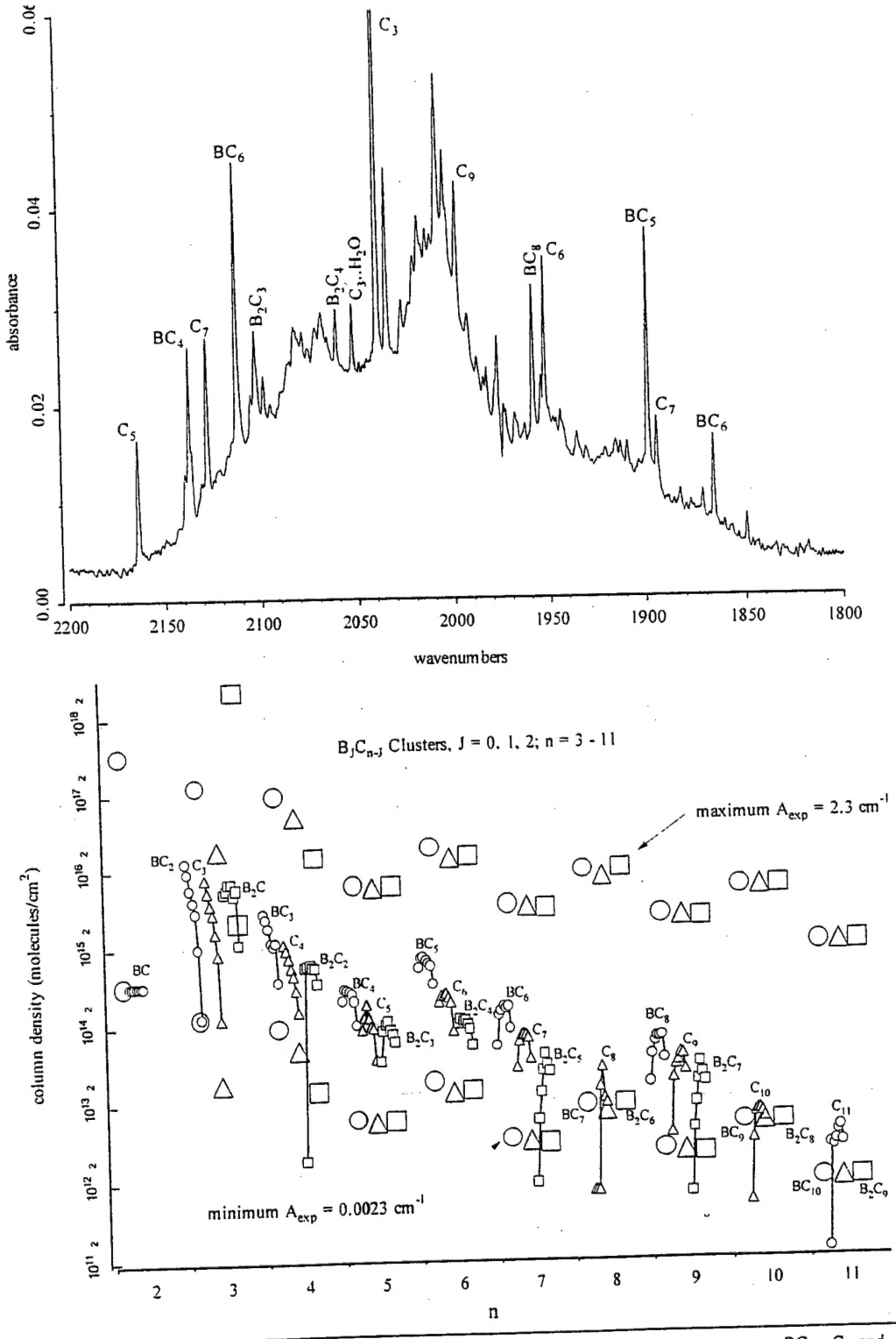
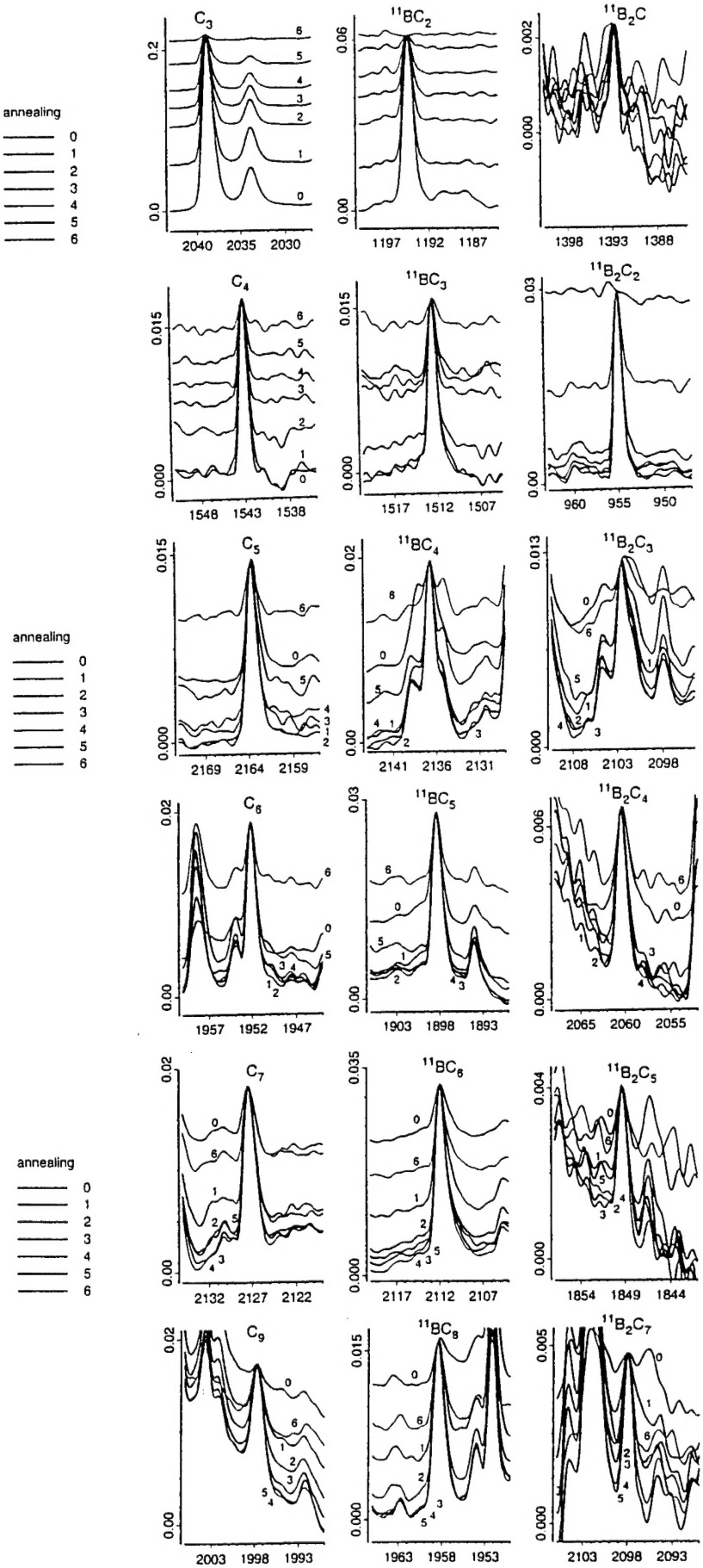
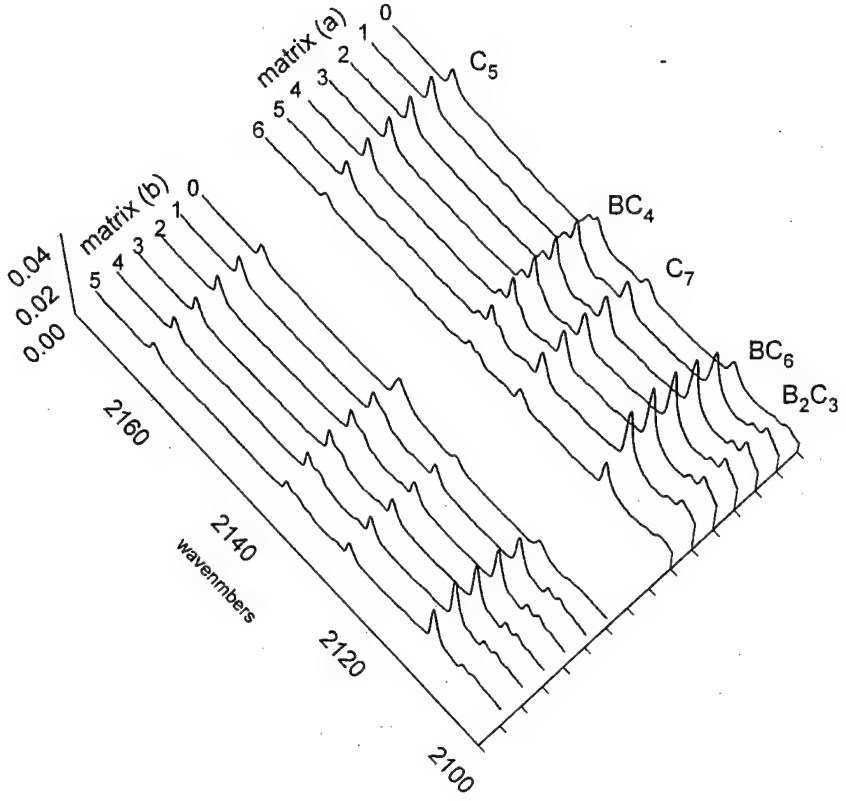


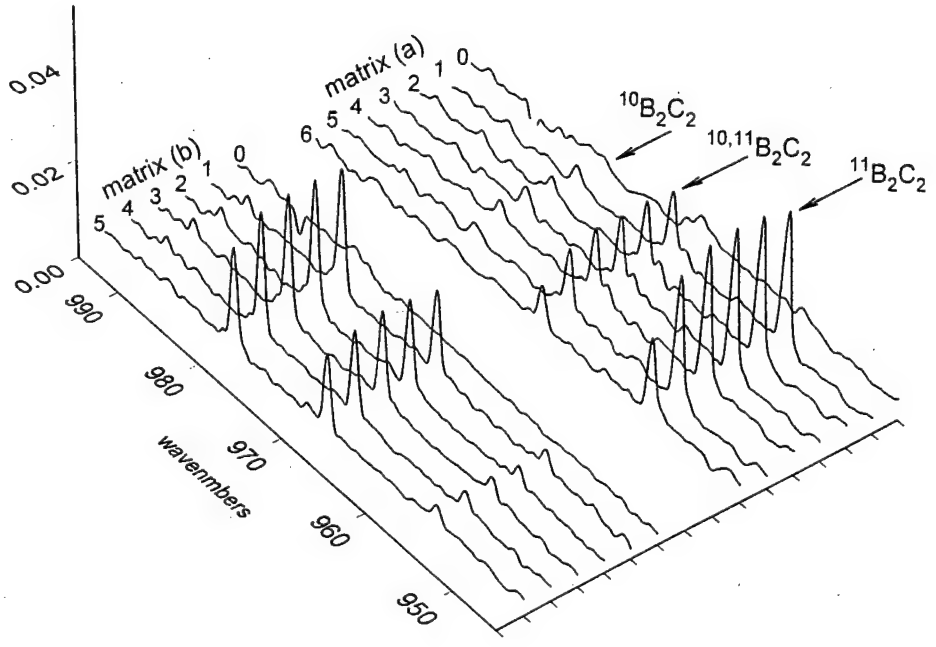
Figure 1. Distribution of B_JC_{n-J} clusters. J = 0, 1, 2; n = 3 - 11. Circles, triangles and squares represent BC_{n-1}, C_n, and BC_{n-2} clusters, respectively. Large symbols denote upper and lower limits of measurement, based on a nominal minimum measurable absorbance of 0.0023 cm^{-1}, and a maximum absorbance for linearity of Beer's law of 2.3 cm^{-1} (1% transmittance. Small symbols denote measured quantities in the initial matrix, and in six annealed matrices. Annealing temperatures and times were (1) 27.5 K/150 s, (2) 30.0 K/75 s, (3) 32.5 K/45 s, (4) 35.0 K/30 s, (5) 37.5 K/20 s, (6) 40.0 K/20 s. The decreases in column density in the fifth and sixth annealing are due to matrix sublimation. Some of the larger clusters (n = 8, 10, 11) have not been identified, BC_7, B_2C_6, BC_9, B_2C_8, BC_{10}, B_2C_9.

matrix (a): $^{11}B/^{10}B$ = 80/20, $^{12}C/^{13}C$ = 99/1

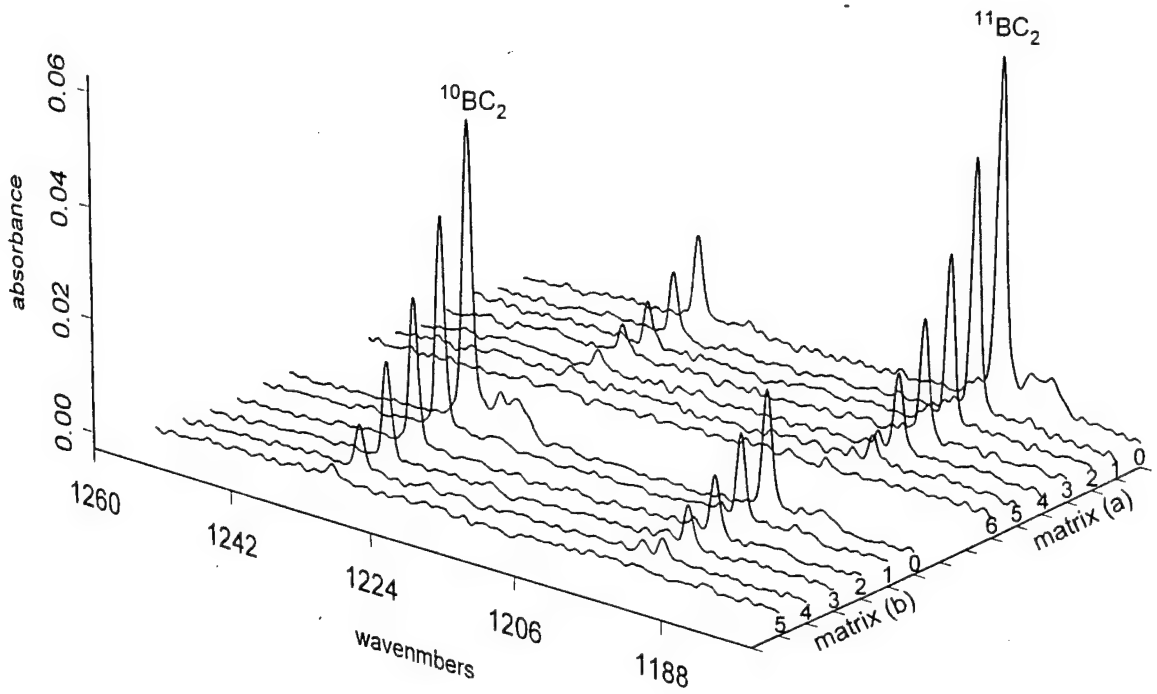




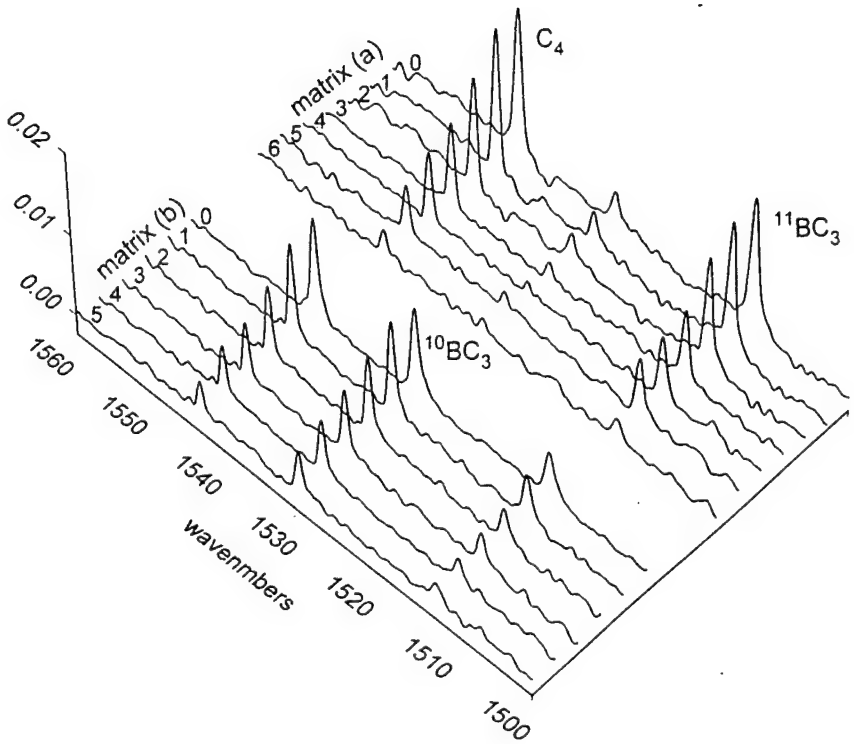
BC6rg3D May 28, 1999 8:32:14 AM



B2C2-3D May 28, 1999 8:31:14 AM



BC2rg3D May 28, 1999 8:28:17 AM



Results and Discussion

Linear C_3, cyclic BC_2, and cyclic B_2C, constituted about 80% of the total observable boron and carbon in the initially deposited matrix, but B_3 was not observed.

The measured trimer distribution in the initially formed matrices was

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1.5 : 0.5 : < 0.05.$$

Statistical substitution of J boron atoms into an n-atom carbon cluster produces a distribution given by $\rho(B_JC_{n-J})/\ \rho(C_n) = [\{n(n\text{-}1)\ldots(n\text{-}J\text{+}1)\}/J!]\ [B/C]^J$. With the experimental B/C ~ 1/3, the statistical trimer distribution is

$$\rho(C_3) : \rho(BC_2) : \rho(B_2C) : \rho(B_3) \sim 1 : 1 : 0.33 : 0.03.$$

Agreement between distributions implies trimers form by random condensation of well-mixed atoms, uninfluenced by the relative energies of the trimers, the energies of their precursors, or preferential kinetics pathways that could otherwise distort the statistics.

Linear C_3 and cyclic BC_2, disappeared entirely when the matrices were repeatedly annealed to temperatures between 25 K and 35 K, but cyclic B_2C was inert.

Linear C_4 and BC_3 (BCCC) disappeared more slowly, and linear B_2C_2 (BCCB) grew to ~ 95% of its final value during the first annealing. B_2C_2 was also inert, as B_2C.

The sources of B_2C_2 are from condensation of atom plus trimer ($B + BC_2$ but not $C + B_2C$) or dimer + dimer ($BC + BC$ but not $B_2 + C_2$). Although BC was not observed, the upper limit of $\rho(BC)$ is larger than $\rho(B_2C_2)$ so that BC cannot be ruled out as a source of B_2C_2.

The growth of B_2C_2 is conclusive evidence of the presence of BC and/or B in the originally deposited matrix in an amount at least as great as the growth of B_2C_2.

Linear C_5, BC_4 (BCCCC) and B_2C_3 (BCCCB)] and larger linear clusters (B_JC_{n-J}, $5 < n < 11$, $J = 0, 1, 2$), all grew upon annealing.

The sources of B_2C_3 are dimer + trimer ($BC + BC_2$ but not $B_2 + C_3$) and atom + tetramer ($B + BC_3$ but not $C + B_2C_2$).

Since $\rho(BC_2) \sim 5\rho(BC_3)$ in the initially deposited matrix, the $BC + BC_2$ source is dominant. Growth of B_2C_3 conclusively establishes the presence of BC in the matrix in an amount at least as great as the amount by which B_2C_3 grows.

Growth of BC_4 occurs primarily by $BC + C_3$ rather than $B + C_4$ or $C + BC_3$ because $\rho(C_3) \sim 10\rho(C_4)$ and $\rho(C_3) \sim 2\rho(BC_3)$. Growth of C_5 occurs by $C + C_4$ and $C_2 + C_3$, which establishes the presence of C and/or C_2 in the original matrix in an amount at least as great as C_5 growth.

Disappearance of triangular BC_2 requires breaking of one of its B-C bonds when one of its carbon atoms is attacked. The major reorganization of electronic energy involved in opening the ring appears to occur with little ($< \sim 3$ kcal mol^{-1}) or no energy barrier, which makes this small molecule a candidate for an interesting *ab-initio* study of unusual reactivity at low temperature.

Goal

Production of Cryogenic HEDM with Five Mole Percent Atoms.

Objective

Development and Characterization of Boron Atom Source.

Approach

Production of HEDM by evaporation of boron with high-temperature graphite furnace and co-deposition of vapor with argon on a cold (10 K) surface

Identification and quantitative analysis of B_JC_{n-J} species ($n \geq 3$, $J = 0$ to n) by FTIR spectroscopy and *ab-initio* calculations

Quantitative measurement of distributions of B_JC_{n-J} species produced upon deposition and after annealing to a constant composition.

Summary

Identities, structures and thermodynamic properties of BC_2, B_2C, BC_3, and B_2C_2 are conclusively established by isotope studies and matching experimental infrared spectra to predictions of theory.

Using the Standard Comparative Scheme adopted for the Isp of HEDM propellants (5 mole percent HEDM molecule in solid hydrogen) the predicted Isp of these new molecules stack up against the standards as follows:

Summary (continued)

Isp(LOX/LH2)	389 sec
Isp(B atom)	482 sec
Isp(B_2)	492 sec
Isp(BC_2)	482 sec
Isp(B_2C)	447 sec
Isp(BC_3)	439 sec
Isp(B_2C_2)	439 sec

Conclusions

Annealing kinetics of disappearance of C_3 and BC_2, and of appearance of B_2C, C_4, BC_3 B_2C_2, C_5, BC_4, and B_2C_3 unequivocally establishes the presence of atoms and dimers in the originally deposited matrix.

~ 80% or more of the initially deposited HEDM existed as atoms, dimers and trimers.

Molecules with two boron atoms are immune from radical attack and condensation during annealing.

Future work

Continued development of source for production of higher flux beam of nearly pure boron atoms.

Map of "islands of stability" of pure boron HEDM; B_2 or B_3 may be the ultimate sink for atoms in the low temperature HEDM environment.

Determine reactivity of boron atoms with hydrogen during co-deposition.

Develop rapid condensation methodology to prevent reaction of B with H_2.